

Determination of Mn valence states in mixed-valent manganates by XANES spectroscopy

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ABSTRACT

The valence states of Mn in mixed-valent layer and tunnel structure manganese dioxides (MnO_2), usually referred to as phyllosmanganates and tectomanganates, can be measured by X-ray absorption near-edge structure (XANES) spectroscopy with a precision and accuracy that are difficult to estimate owing to the paucity of well-characterized standards. A compilation of the Mn K -edge XANES spectra of most naturally occurring manganates, synthetic analogs of known structure and chemical composition, and pure-valence phase species is presented and made available as an open source. We intend this compilation to serve as a basis for the spectroscopic determination of the fractions of the Mn $2+$, $3+$, and $4+$ valences in mixed-valent manganates and phase mixtures. The XANES derivatives of tectomanganates and phyllosmanganates with no or little Mn^{3+} in the MnO_2 layer exhibit intensities, shapes, and relative energy positions of the main features characteristics of a particular valence composition. For these compounds, valence fractions can be derived using linear combination fitting analysis. Best quantitative results are obtained when the unknown spectrum is fit to a weighted sum of all reference spectra in the database with the fractions of species constrained to be non-negative (Combo method). The accuracy of the average valence is estimated to 0.04 v.u. in the range of $3+$ to $4+$, and decreases when the proportion of divalent Mn is higher than 15%. The accuracy of the method is also lower in (layer Mn^{3+} , Mn^{4+}) manganates, because the XANES features are affected non-additively by the amount and distribution of the Jahn-Teller Mn^{3+} cations. The merit of the Combo method for the determination of manganese valence sums relative to the methods based on calibration curves is discussed.

Keywords: XANES, valence determination, phyllosmanganates, tectomanganates, manganese oxides

INTRODUCTION

Manganates of nominal stoichiometry MnO_2 exist in many polymorphic forms and over a wide compositional range (Fig. 1). Layered manganates are commonly referred to as phyllosmanganates or as birnessite-type compounds and those with a tunnel framework structure as tectomanganates. Apart from the two stoichiometric forms pyrolusite ($\beta\text{-MnO}_2$) and ramsdellite, which have tunnel dimensions of 1×1 and 2×1 , respectively, all manganates have a charge deficit arising from low-valent manganese substitutions or from octahedral Mn vacancies that is balanced by various types of cations, such as alkali and alkaline earth metal ions (e.g., Li, K, Rb, Cs, Ca, Ba, Ra) and hydrolyzable cations (e.g., Ni, Zn, Pb). The redox and sorption properties of manganates give them a decisive role in several biological systems, environmental processes, and technological applications. For example, phyllosmanganates can be intercalated with various organic and inorganic compounds to form multilayer nanocomposites or pillared structures. They are widely used also as templates for the formation of octahedral molecular sieves with variable tunnel sizes that have demonstrated excellent properties in heterogeneous catalysis, hazardous waste remediation, and rechargeable battery technology (Thackeray 1997; Toupin et al. 2004; Wang et al. 2004, 2005, 2011; Cormie et al. 2010;

Laatikainen et al. 2010; Lafferty et al. 2010; Nakayama et al. 2010; Tang et al. 2010; Yan et al. 2010, 2011; Kim et al. 2001; Pinaud et al. 2011).

Natural and synthetic manganates often involve mixtures of up to three valences (Mn^{2+} , Mn^{3+} , Mn^{4+}), which may coexist in a single mixed-valent phase or be distributed between several species in a mixture. In both cases, it is therefore important to be able to determine the proportions of each valence state in situ, as opposed to measuring the average valence, for example by wet chemistry (Lingane and Karplus 1946; Vetter and Jaeger 1966). This information can be obtained from the analysis of the manganese $L_{2,3}$ and oxygen K -edges using electron energy loss near-edge (ELNES) or X-ray absorption near-edge structure (XANES) spectroscopy (Kurata and Colliex 1993; Mansot et al. 1994; Garvie and Craven 1994b; Bridges et al. 2000, 2001; McKeown and Post 2001; McKeown et al. 2003; Gilbert et al. 2003; Pecher et al. 2003; Glatzel et al. 2004; Riedl et al. 2006; Loomer et al. 2007; Ito et al. 2011). Several methods have been proposed. Among them, the two that seem to work best are: (1) the difference between Mn L_3 and oxygen K energies, i.e., $\Delta E(\text{Mn } L_3\text{-O } K)$ vs. valence; and (2) a linear combination fit (LCF) to a set of pure-valence references (Zhang et al. 2010). The accuracy for the quantification of average Mn valence in the range of $3+$ to $4+$, estimated from a set of synthetic cryptomelane (2×2 tectomanganate) standards, can be as good as ± 0.02 valence units (v.u.) with the first method and ± 0.03 with the second. However,

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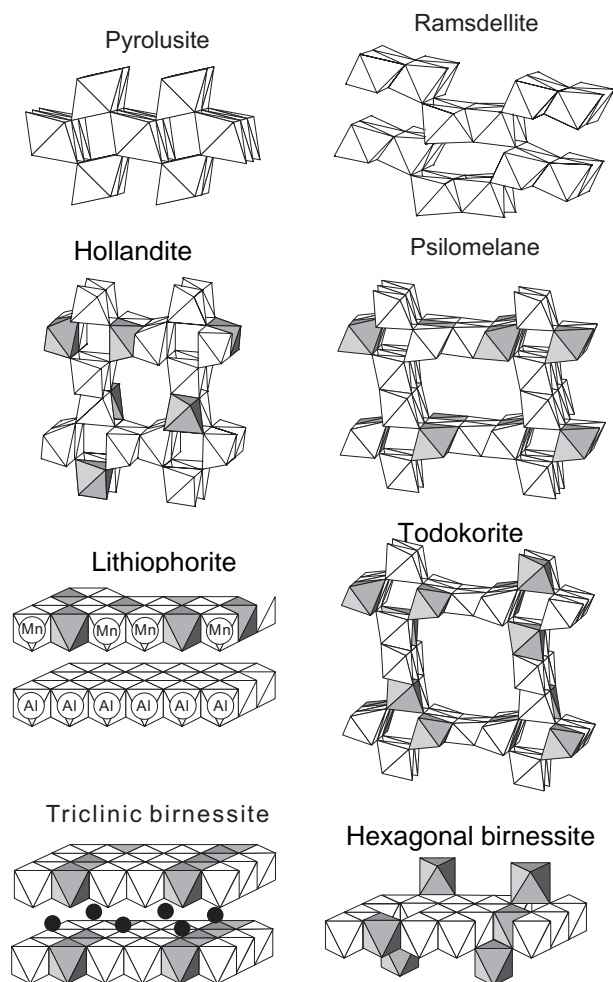


FIGURE 1. Polyhedral representation of the main types of tectomanganates (pyrolusite, ramsdellite, hollandite, psilomelane = romanechtite, todokite) and phyllosilicates (birnessite, lithiophorite). Octahedra occupied by Mn³⁺ cations are in gray.

as powerful as these methods are, none of them separately or together is totally satisfying. The error of the $\Delta E(\text{Mn } L_{3-2} \text{ O } K)$ calibration curve is larger in the presence of other heterovalent cations such as Fe³⁺, a common impurity in natural materials, because the position of the oxygen *K*-edge is affected by all oxygen bonding environments in the structure, including those in any waters of hydration. Results depend also to some extent on the selection of the assumed end-members (e.g., pyrolusite vs. ramsdellite), presumably because various arrangements of Mn octahedra give rise to different shapes of ELNES spectra (Zhang et al. 2010), as reported for XANES (Manceau et al. 1992). The slightly lower accuracy of the LCF method relative to $\Delta E(\text{Mn } L_{3-2} \text{ O } K)$ (± 0.03 vs. ± 0.02) is, however, somehow compensated by its ability to estimate the fraction of Mn²⁺, in addition to Mn³⁺ and Mn⁴⁺ from the weight of each fit component, provided the appropriate reference spectra are chosen.

The valence states of Mn in mixed-valent manganates can be obtained also by *K*-edge XANES spectroscopy (Manceau et al.

1992; Amundsen et al. 1998; Ressler et al. 2000; Jokic et al. 2001; Villalobos et al. 2003; Ramallo-Lopez et al. 2004; Gunter et al. 2002, 2004, 2006; Bargar et al. 2005; Farges 2005; Figueroa et al. 2005; Negra et al. 2005; Webb et al. 2005; Saratovsky et al. 2006; Chaboy 2009; Chalmin et al. 2009; Grangeon et al. 2010; Rumble et al. 2010). Considering the large variability in structural and chemical compositions of manganates, not easily accessible to measurement, one might then ask whether there are features of the XANES that are independent enough of the exact species to be useful in quantitating mixtures and heterovalent manganates. This first question was addressed by recording high-quality XANES spectra from a large series of well-characterized Mn compounds (Table 1), which include many of the distinct stoichiometries and polyhedral arrangements described in the literature, and by defining “valence state fingerprints” from the spectral derivatives that are ideally unique to specific Mn oxidation and almost independent of the manganate structure.

The identification of valence state fingerprints leads to the second question of whether they are distinct enough to determine, with good precision, the fractions of each valence in a mixed-valent system. To answer this question, the XANES spectra of aliovalent manganates with known structure and chemical formula were fit to linear combinations of pure Mn species. We show that the unknown amounts of Mn 2+, 3+, and 4+ can be obtained when: (1) the whole set of pure-valence references is included in the LCF, regardless of their chemical and polyhedral similarity with the unknown; (2) all unphysical negative loadings of the references are rejected from the regression; and (3) the *n*+ fraction in the unknown is taken as the sum of all positive fractions obtained for the *n*+ references (*n* = 2, 3, 4). The accuracy of the proposed method for tectomanganates and phyllosilicates containing no or little Mn³⁺ in the layer and less than ~15% Mn²⁺ is 0.04 v.u., as determined by applying this method to well-characterized mixed-valent materials, therefore close to that obtained with ELNES. However, this method presents the advantage of not requiring educated choices on the relevance of a particular reference used in the LCF. Finally, by making the database openly available as [Supplementary material¹](#), we aim

TABLE 1. List of pure-valence references

Standard	Code name	Formula	Mn valence	Source/Reference
Pyrolusite	REF4-1	β-MnO ₂	4.0	Nassau, Germany
Ramsdellite	REF4-2	MnO ₂	4.0	
Ca ₂ Mn ₃ O ₈	REF4-3	2/3 Ca ₂ Mn ₃ O ₈ + 1/3 CaMnO ₃	4.0	Gaillot et al. (2005)
KBi	REF4-4	K _{0.296} (Mn _{0.926} ⁴⁺ Mn _{0.074} ³⁺)O ₂ · 0.40H ₂ O	4.0	
Groutite	REF3-1	α-MnOOH	3.0	Minnesota, U.S.A.
Feitknechtite	REF3-2	β-MnOOH	3.0	
Manganite	REF3-3	γ-MnOOH	3.0	Manceau et al. (1992)
Mn ₂ O ₃	REF3-4	Mn ₂ O ₃	3.0	
MnPO ₄	REF3-5	MnPO ₄	3.0	Grangeon et al. (2010)
Hureaulite	REF2-1	Mn ₃ (PO ₄) ₂ (OH) ₂ · 4H ₂ O	2.0	
Fungi	REF2-2	Mn ²⁺ -sorbed fungi	2.0	Manceau and Gallup (2005)
Rhodocrosite	REF2-3	MnCO ₃	2.0	
Manganosite	REF2-4	MnO	2.0	Manceau and Gallup (2005)
Pyroxmangite	REF2-5	(Mn,Fe)SiO ₃	2.0	
Tephroite	REF2-6	Mn ₂ SiO ₄	2.0	Manceau and Gallup (2005)
MnSO ₄ aq	REF2-7	Solvated Mn ²⁺ , aqueous solution	2.0	
MnSO ₄ s	REF2-8	MnSO ₄ · xH ₂ O	2.0	Alfa Aesar-010807

Note: = vacancy.

to provide a useful resource for others.

EXPERIMENTAL METHODS

Measurements

All spectra are from beamline 10.3.2 at the Advanced Light Source and were acquired with procedures similar to those described in Marcus et al. (2008). The energy was referenced to the first inflection point in metallic Mn at 6537.7 eV (Kraft et al. 1996). With this calibration, the second peak in the derivative of the signal occurs at 6540.9 eV for Mn^{3+} and Mn^{4+} compounds. The uncertainty in energy is 0.1 eV. To facilitate normalization and possibly make use of EXAFS-region information, data were taken out to 300 eV above the edge.

To reduce overabsorption, many of the references were run in total electron yield mode. For others, fluorescence yield was used on small particles and the consistency of results checked from particle to particle. In some cases, there were inter-particle variations that could not be ascribed to varying amounts of overabsorption; they were attributed to dichroism in single-crystal grains, so we used the average over several particles in the database. Radiation damage was checked for by comparing successive scans on a spot. For some samples, QuickXANES was used to acquire data with minimal beam damage per spot. For the aqueous MnSO_4 solution (1 wt% in DI water), the microprobe beam caused the accumulation of Mn at the irradiated spot; closing down slits in front of the focusing mirrors allowed us to attenuate the beam enough to let us use QuickXANES to get consistent spectra without this radiation-induced accumulation.

Data handling

The data were deadtime-corrected, energy calibrated, pre-edge subtracted and post-edge normalized, and analyzed using the software available from the beamline web site. The pre-edge subtraction and post-edge normalization procedures are shown in Supplementary Figure 1¹. The reliability of the linear-combination method was verified by fitting the data from mixed-valent compounds in the ranges between 6521–6653 and 6535–6570 eV.

RESULTS AND DISCUSSION

Valence states fingerprint

Among the 17 reference spectra, the energy at which the absorption rises to half its post-edge value increases by 3.3 ± 0.9 eV from Mn^{2+} to Mn^{3+} and by 3.0 ± 0.6 eV from Mn^{3+} to Mn^{4+} (Fig. 2a). With a precision on the energy measurement of ± 0.1 eV, this chemical shift allows differentiation of the three oxidation states in single-valent samples. Quantitative analysis of multicomponent spectra from polyvalent samples is, however, clearly hindered by the large variability among spectra from the same valence group, especially for the $2+$ group. It is preferable to work with the first derivative of the absorbance ($d\mu/dE$) because it generally shows the spectroscopic structure more clearly than the absorption spectrum, and small errors in the post-edge normalization do not change the shape of the derivative (Fig. 2b).

The (Mn^{3+} , Mn^{4+}) manganate spectra from the database show that trivalent Mn is reflected phenomenologically on the first derivative in a decrease of the amplitude at 6555.0–6560.0 eV from the Mn^{4+} component, and an increase at 6547.9–6549.0 eV from the Mn^{3+} component (Fig. 3a). For example, the spectrum for todorokite_{SAF}, with a nominal mean valence of 3.73 (Table 2) (Post et al. 2003), is intermediate between those of the Mn^{4+} phyllomanganate reference KBi and the Mn^{3+} references groutite

(α - MnOOH) and feitknechtite (β - MnOOH ; Fig. 3b). Comparison of the spectra for 2×2 (hollandite), 2×3 (psilomelane), and 3×3 (todorokite) tectomanganates shows that the ratio of the amplitudes at the two “indicator” regions is sensitive to a variation of a few hundredths valence units (v.u.) (Fig. 4a; Table 2). The best two-component fit of the todorokite_{SAF} derivative was obtained with $0.58 \text{ KBi} + 0.37 \beta\text{-MnOOH}$, corresponding to the unrealistically low average valence of 3.58–3.61 (Fig. 5a). This low value and the relatively poor quality of the fit, with a normalized sum-squared residual (NSS) of $3.7 \cdot 10^{-2}$, show that the Mn *K*-edge spectra of tectomanganates cannot be modeled as weighted sums of only two end-member spectra.

Divalent Mn in (Mn^{2+} , Mn^{3+} , Mn^{4+}) manganates is indicated on the XANES derivative by a leftward shift of the rising slope at 6542–6547 eV relative to tectomanganates and (Mn^{3+} , Mn^{4+}) phyllomanganates (Figs. 3c, 4b, and 4c). Using hexagonal birnessite HBi5 as a three valence state reference, the visual detection limit of Mn^{2+} is about 5% of the total Mn (Table 2).

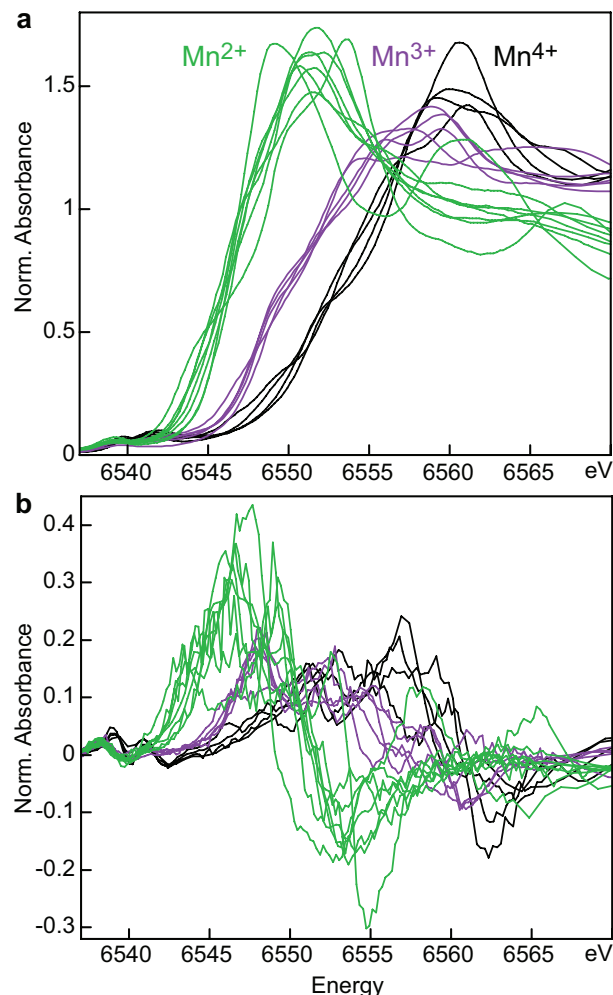


FIGURE 2. XANES absorption spectra (a) and first derivatives (b) of single-valent Mn^{2+} , Mn^{3+} , and Mn^{4+} species in the database. For clarity, spectra are not identified individually, but can be freely downloaded from the supplementary materials¹.

¹ Deposit item AM-12-037, Supplementary data, tables, and figures in PDF and two ASCII files (Mn XANES database). Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

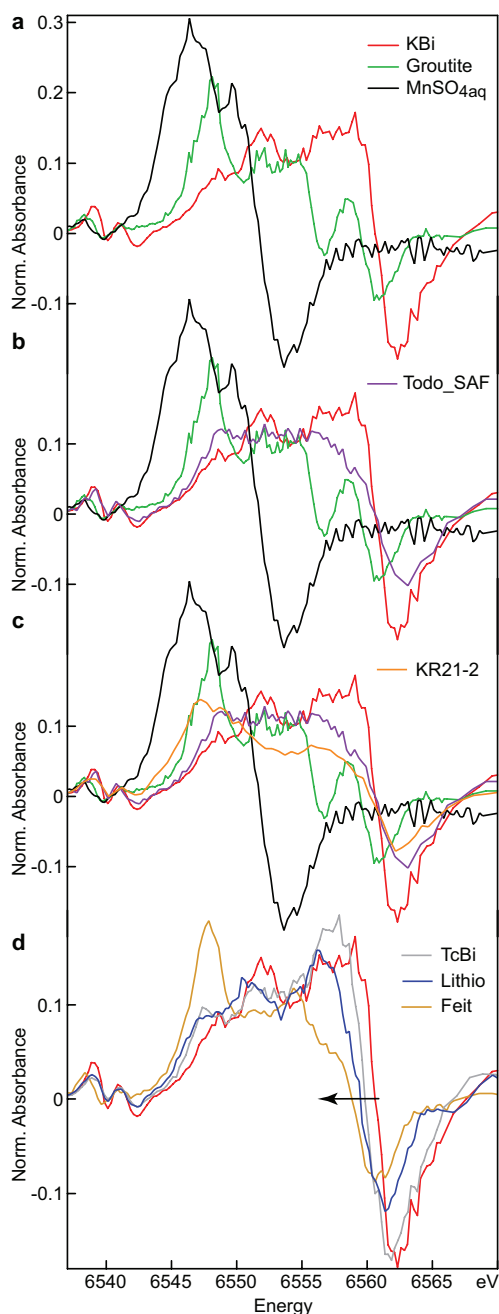


FIGURE 3. First derivative XANES absorption spectra of a selection of single- and mixed-valent Mn species.

This diagnostic spectral feature is not captured when the HBi5 spectrum is reconstructed with a linear combination of pure-valence (phyllo-, tecto-) manganate species. The best model-fit with three components from the entire database yields 0.21 ramsdellite (Mn^{4+}) + 0.38 KBi (Mn^{4+}) + 0.37 β -MnOOH ($NSS = 1.8 \cdot 10^{-2}$), that is 59–61% Mn^{4+} and 37–39% Mn^{3+} , in disagreement with the nominal composition of $\text{Mn}_{0.722}^{4+}\text{Mn}_{0.22}^{3+}\text{Mn}_{0.055}^{2+}$ (Fig. 5b) (Lanson et al. 2000).

So far, all examined mixed-valent manganates exhibited in-

termediate spectral features that could be explained empirically by direct comparison with end-members. This is not the case when Mn^{3+} , a Jahn-Teller cation, is incorporated in the manganese layer, as in triclinic birnessite (TcBi) and lithiophorite, and not dominantly in the interlayer, as in HBi. TcBi and lithiophorite have a maximum at 6556.3–6558.0 eV, which is absent from KBi8 and β -MnOOH, the two closest phylломanganate end-members (Fig. 3d). In addition, TcBi and lithiophorite have distinct derivatives, although similar amounts of layer Mn^{3+} : 31% and 33%, respectively. The layer strain induced by the Jahn-Teller effect is reduced in TcBi by the ordering in rows of the Mn^{3+} ions among the lattice of Mn^{4+} , the stripe layer having an orthogonal symmetry (Drits et al. 1997; Lanson et al. 2002). In contrast, the layer distortion is reduced in lithiophorite by the avoidance of Mn^{3+} -O- Mn^{3+} links resulting in an even distribution of the two types of cations and a hexagonal symmetry of the layer (Manceau et al. 2005). These defects, and their minimization, affect the structure, and thus the XANES, in a non-additive way relative to the Mn^{4+} -pure and Mn^{3+} -pure end-members. Synergistic effects of various defects on the structure and XANES also occur in manganites (Chaboy 2009). Although the XANES spectra of (layer Mn^{3+} , Mn^{4+}) phylломanganates cannot be modeled, even semi-quantitatively, as a weighted sum of single-valence end-members, they have distinctive spectral features that can be used to speciate Mn in unknown materials. One of those is a leftward shift of $d\mu/dE = 0$ in the 6559.0–6560.5 eV interval with increasing Mn^{3+} in the layer (Fig. 3d).

In summary, Mn *K*-edge XANES is sensitive to the oxidation state and bonding environment of Mn in polyvalent manganates, and spectral fingerprints were defined that can be used to speciate the manganese forms in an unknown compound. However, the assumption that the XANES of mixed-valent manganates can be modeled simply by weighting the spectra of the structurally and chemically closest end-members does not hold. Is quantification nonetheless possible? Principal component analysis (PCA) with target transformation (TG) (Weiner et al.

1970; Hopke 1989; Malinowski 1991; Wasserman et al. 1999; Ressler et al. 2000; Manceau et al. 2002) are applied next, to determine which combination of pure-valence species may provide the correct valence composition in a mixed-valent manganate, if any.

Principal component analysis

The analysis was applied on the 12 mixed-valent tectomanganates and phylломanganates with no or little layer Mn^{3+} , because their XANES are least affected by the short- and medium-range ordering of Mn (Table 2). The output parameters, including eigenvalues, the variance, the Malinowski (1977) indicator values (IND), and the variation of the fit total (normalized total sum-squared residual, NSS_{Tot}), are given in [Supplementary Table 1¹](#) for the six most significant principal components (PCs).

The decline of the eigenvalues, which ranks PCs according to their importance in reproducing a data set, and IND, which usually reaches a minimum for the least significant component, both identified three PCs (Supplementary Fig. 2 and Table 1¹). The first component represents features common to all spectra and has approximately the same loading for all spectra. This component accounts for 85.8% of the “strength” of the deriva-

TABLE 2. List of mixed-valent compounds

Compound	Formula	Average Mn valence		Source/Reference
		Formula	Titration*	
Tectomanganate				
Hollandite			3.75–3.83†	Fron del et al. (1960)
Psilomelane‡			3.75–3.75†	Hufgard, Germany
Todorokite_Japan			3.72–3.73†	
Todorokite_SAF	Mg _{0.45} Na _{0.42} Ca _{0.15} K _{0.01} (Mn _{4.38} ⁴⁺ Mn _{1.62} ³⁺)O ₁₂ ·4H ₂ O	3.73		South Africa, Post et al. (2003)
Phyllomanganate with no/little layer Mn ³⁺				
KBi8	K _{0.231} Mn _{0.077} ³⁺ (Mn _{0.885} ⁴⁺ _{0.115})O ₂ ·0.6H ₂ O	3.92	3.87	Gaillot et al. (2003)
HBi5	Mn _{0.11} ³⁺ Mn _{0.055} ²⁺ H _{0.33} (Mn _{0.722} ³⁺ Mn _{0.11} ⁴⁺ _{0.167})O ₂ ·0.5H ₂ O	3.66		Silvester et al. (1997); Lanson et al. (2000)
KR21–2	Mg _{0.04} K _{0.03} Mn _{0.25} ³⁺ (Mn _{0.78} ⁴⁺ _{0.22})O ₂ ·nH ₂ O\$ Mn _{0.15(5)} ²⁺ Mn _{0.10(10)} ³⁺ Mn _{0.73(10)} ⁴⁺			Fungal phyllomanganate, Grangeon et al. (2010)
KR21–Cu-A, B				Fungal phyllomanganate treated with 10 mM CuSO ₄ (A) and rad-damaged (B).
SP6–Cu-A, B, C				Bacterial phyllomanganate treated with 10 mM CuSO ₄ (A) and rad-damaged (B, C).
Phyllomanganate with layer Mn ³⁺				
KBi10	K _{0.314} (Mn _{0.737} ⁴⁺ Mn _{0.246} ³⁺ _{0.017})O ₂ ·0.5H ₂ O	3.75	3.67	Gaillot et al. (2007)
TcBi	Na _{0.31} (Mn _{0.69} ⁴⁺ Mn _{0.31} ³⁺)O ₂ ·0.4H ₂ O	3.69		Lanson et al. (2002)
Lithiophorite	(Al _{0.67} Li _{0.32})(Mn _{0.68} ⁴⁺ Mn _{0.32} ³⁺)O ₂ (OH) ₂	3.68	3.67–3.67†	Manceau et al. (2005)
Other				
Hausmannite	Mn ₃ O ₄	2.67		

* Potentiometric titration using (NH₄)₂Fe(SO₄) Mohr salt and sodium pyrophosphate (Lingane and Karplus 1946; Vetter and Jaeger 1966). † = vacancy.

‡ Duplicate.

§ Fraction of Mn²⁺ = 0.05. Also named romanechite.

|| From X-ray diffraction. This technique is not sensitive to residual Mn²⁺ not oxidized by fungi.

|| Bulk fractions of Mn 2+, 3+ and 4+ from XANES, with estimated uncertainty in parenthesis.

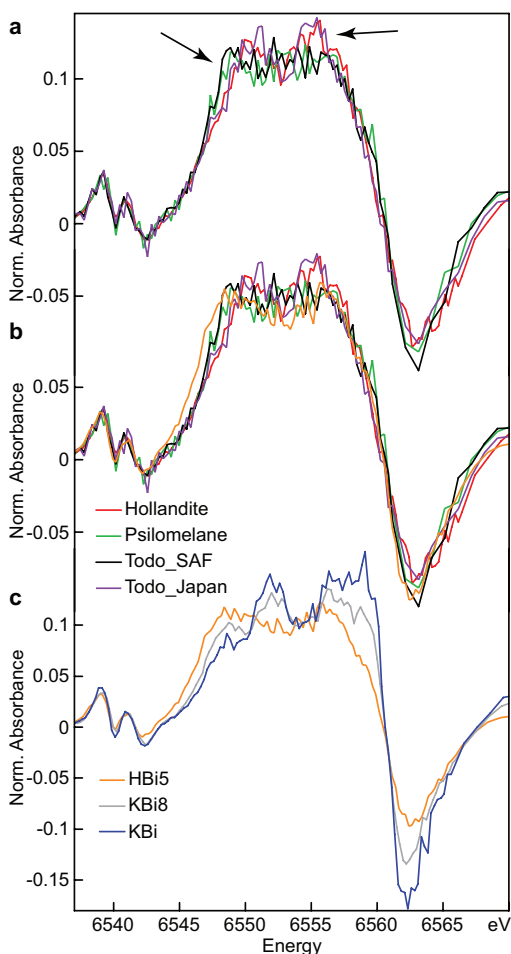


FIGURE 4. First derivative XANES absorption spectra of phyllomanganates and tectomanganates with various proportions of Mn²⁺ and Mn³⁺.

tive signal. The other 14.2% is the contribution from differences (i.e., variance) between spectra including noise. The next two components account for $13.1 + 0.8 = 13.9\%$. That is, the sum-squared (norm) of the part of the reconstructed signal that comes from the second and third component is 13.9% of the whole, which is $13.9/14.2 = 98\%$ of the variance between XANES derivative spectra.

Deviations between data and reconstructions based on three PCs were small with normalized sum-squared (*NSS*) values from 2.4 to $8.3 \cdot 10^{-3}$, and a *NSS-Tot* of $5.4 \cdot 10^{-3}$. Therefore, the series of manganates can be described well with variable proportions of only three model compounds, which theoretically can be identified from a database by target transformation, provided the unknown is present in the library of reference spectra. Target testing of a reference goes beyond the fingerprinting approach between known and unknown spectra, because the entire data set is analyzed at one time in a statistically meaningful way for similarity to a specific structural reference. This similarity was evaluated with the normalized sum-squared residual (*NSS*) between the tested reference and its target transform, and with the *SPOIL* value (Malinowski 1978). Usually, references with *SPOIL* values <1.5 are considered excellent, 1.5 to 3 good, 3 to 4.5 fair, 4.5 to 6 poor, and >6 unacceptable.

Out of the 17 pure species contained in the database, one Mn⁴⁺ reference fell into the *SPOIL* category excellent (KBi), and three were fair to poor (Supplementary Table 2 and Fig. S3¹). Neither groutite (α -MnOOH, 2×1 tunnel structure) nor manganite (γ -MnOOH, 1×1) passed the test successfully, although they were supposedly a good structural proxy for tectomanganates and for phyllomanganates with interlayer Mn³⁺ octahedra bonded by shared corners to the manganese layer. This result explains why the valence composition of todorokite_SAF and HBi5 could not be obtained previously from a two- or three-component unconstrained fit of all the pure-valence references

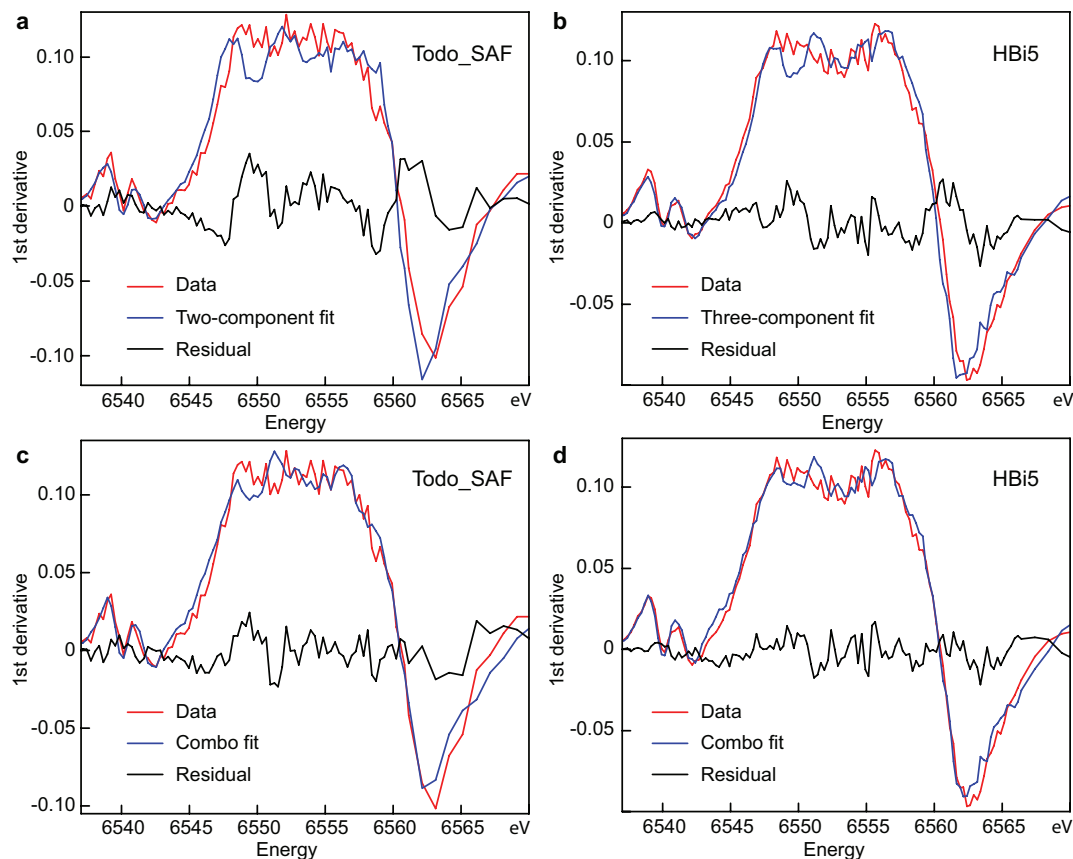


FIGURE 5. (a) Best two-component fit of todorokite_SAF. (b) Best three-component fit of HBi5. (c and d) Same spectra fitted with the Combo method.

in the database. More generally, the above exercise shows that there are not really idealized Mn^{2+} , Mn^{3+} , and Mn^{4+} spectra that can be mixed in various proportions to model the spectra of real mixed-valent materials. As will be shown below, the valence fractions and average oxidation state can be obtained when all pure-valence species are included in the fit, so as to include in the regression all distinct bonding environments contained in the database and plausibly present in the unknown.

Linear combinations with a database of pure-valence species (the Combo method)

Some methods for analyzing valence states, such as fitting the pre-edge peaks, rely on a few features of a small region of the spectrum (Farges 2001; Galois et al. 2001; Petit et al. 2001; Wilke et al. 2001; Berry et al. 2003). Such methods tend to do well in classifying single species by valence, or extracting the average valence, but are less able to extract the fractions of multiple valence states, as the case with manganese (Farges 2005; Chalmin et al. 2009). Part of the reason for this is that the spectra of different species with a given valence can look quite different. To solve the difficult problem of quantifying multiple valence states, it seems necessary to use as much information as possible, thus the whole spectrum out to some reasonable distance from the main edge. Also, because there is a significant variability between species with the same valence, any purely

empirical method must be developed with reference to as large a set of known references as possible.

Consider the following proposed method: Fit the unknown spectrum to a linear combination of all the reference spectra, and evaluate the fraction of Mn in, say, the Mn^{2+} state as the sum of fractions of each species in the fit times the fraction of divalent Mn in each species. It is tautologically obvious that if the unknown is actually one of the references, the correct answer will be obtained. Furthermore, a spectrum corresponding to a mixture of known references will “read” as a valence mixture appropriate to the input mix. Thus, this method works perfectly to “interpolate” between known references. If this method is applied to a true unknown, it will often yield unphysical negative loadings (fractions of species) for many of the references. If, for instance, two of the references are similar to each other, one can get loadings of opposite sign and large and almost equal magnitude, as the fit “tries” to work with the small difference between the two references. Furthermore, the fits become very noisy because the fitting problem is ill-conditioned. To avoid these problems, we have to constrain the loadings to be non-negative.

We applied this non-negativity constraint in two different ways and obtained the same results. In one method, we did an unconstrained linear fit to a sum of all the references, and then progressively eliminated references with negative loadings in ascending order of loading. Note that when one component is

eliminated, the loadings of all others change. After all negative loadings were eliminated, each reference previously deleted was reselected randomly one-by-one to ensure that the global minimum was found rather than a local minimum using *NSS* as best-fit criterion (Supplementary Fig. S4¹). In the other method, we tested all combinations of six or fewer references with positive loadings and chose the one that gave the best fit. The choice of six for the maximum number of components was governed simply by practical limits of the algorithm used. Because both procedures yielded identical or near-identical results, we refer to both as the Combo method. Changing the fit interval had little effect on the results from the derivatives [$\Delta(\text{val}) = 0.01$ v.u.; Supplementary Tables 2 and 3¹], but changed the results from the XANES absorption spectra by as much as 0.03 v.u. due to some inevitable arbitrariness in the slope of the post-edge line during data normalization. This affect was compensated by including a post-edge slope as a free parameter for XANES data fitted in the 6521–6653 eV interval. A measure of the internal consistency of the method can be obtained by comparing the results from the XANES spectra and their derivatives. The differences between average valences derived using the two forms of the spectra is 0.01 v.u. for (Mn^{3+} , Mn^{4+}) manganates, and 0.03–0.08 v.u. when the fraction of Mn^{2+} is higher than ~0.15 (Table 3 and Supplementary Table 4¹).

The spectral fingerprints defined previously on derivatives are reproduced in the fits (Figs. 5c and 5d), and the average valences and fractions now coincide to at least 0.08 and often within 0.03–0.04 with chemical and structural values where available (Table 3 and Supplementary Table 5¹). The greatest differences between XANES-estimated and predicted Mn valences are observed with the birnessites HBi5 (0.05 v.u.) and KBi8 (0.08 v.u.), and may be real because birnessites are metastable (Gaillot et al. 2004) and their structural formulas were established 9 to 12 years ago (Lanson et al. 2000; Gaillot et al. 2003). Indeed,

the ratio of interlayer Mn^{3+} to layer Mn^{4+} of phyllosulfates increases with aging (Grangeon 2009) and they tend to transform into tectomanganates with time (Cui et al. 2010). We conclude that the accuracy for determination of average Mn valence for the range of 3+ and 4+ by the Combo method is 0.04 v.u.

One may ask what the error bars are on the fractions of each reference species (Supplementary Tables 2 and 3¹), and attempt to derive them using the usual statistical methods. However, there is a conceptual problem with this approach to error estimation. Unlike in the usual sort of linear combination fitting, we do not assert that the unknowns are actually mixtures of the reference materials or even of materials that are structurally like the references, nor do we assert that the fits we get are always good representations of the data. In fact, some of the fits (e.g., for hausmannite, *vide infra*)

are quite poor. Therefore, it makes no sense to assign error bars to the loadings of individual components. Rather, what we contend is that the empirical method described here yields the correct average valences to within about 0.04 v.u. in tectomanganates and phyllosulfates containing no or little Mn^{3+} in the layer and less than ~15% Mn^{2+} , and the correct fractions of the valence states to within 4.4% ($\sigma = 2.6\%$; Table 3) and 4.6% ($\sigma = 2.9\%$; Supplementary Table 4¹), when applied to the collection of mixed-valent materials available to us.

Application of the Combo method to the photo-reduction of Mn^{4+} to Mn^{2+} in phyllosulfates

Poorly crystallized phyllosulfates, either biogenic or abiotic, are highly sensitive to electron (Garvie and Craven 1994a) and X-ray (Bargar et al. 2005) beam-induced damage (Manceau et al. 2002). In this process, Mn^{4+} is reduced to Mn^{2+} , but uncertainty remains if the reduction proceeds in one step (i.e., two-electron transfer) or two steps (i.e., two sequential one-electron transfers) via the transient formation

TABLE 3. Fractional and average valence states of Mn obtained from the Combo fit of XANES spectra and derivatives in the 6535–6570 eV interval

	Fractional Mn^{4+}		Fractional Mn^{3+}		Fractional Mn^{2+}		Average Mn valence	
	XANES	Structure	XANES	Structure	XANES	Structure	XANES	Structure/Titration
XANES								
Hollandite	0.81	–	0.19	–	–	–	3.81	3.75–3.83
Psilomelane	0.76	–	0.24	–	–	–	3.76	3.75–3.75
Todorokite_Japan	0.77	–	0.23	–	–	–	3.77	3.72–3.73
Todorokite_SAF	0.70	0.73	0.30	0.27	–	–	3.70	3.73
KBi8	0.84	0.92	0.16	0.08	–	–	3.84	3.87–3.92
HBi5	0.66	0.72	0.29	0.22	0.05	0.05	3.61	3.66
KR21–2	0.58	–	0.28	–	0.14	–	3.45	–
KR21–Cu–A	0.76	–	0.16	–	0.08	–	3.67	–
KR21–Cu–B	0.06	–	0.61	–	0.33	–	2.73	–
SP6–Cu–A	0.71	–	0.13	–	0.16	–	3.56	–
SP6–Cu–B	0.11	–	0.53	–	0.36	–	2.76	–
SP6–Cu–C	0.03	–	0.39	–	0.59	–	2.44	–
First derivative								
Hollandite	0.82	–	0.16	–	0.02	–	3.81	3.75–3.83
Psilomelane	0.81	–	0.16	–	0.04	–	3.77	3.75–3.75
Todorokite_Japan	0.78	–	0.21	–	0.01	–	3.78	3.72–3.73
Todorokite_SAF	0.75	0.73	0.23	0.27	0.03	–	3.72	3.73
KBi8	0.84	0.92	0.14	0.08	0.01	–	3.83	3.87–3.92
HBi5	0.69	0.72	0.24	0.22	0.07	0.05	3.62	3.66
KR21–2	0.61	–	0.23	–	0.16	–	3.45	–
KR21–Cu–A	0.78	–	0.12	–	0.11	–	3.67	–
KR21–Cu–B	0.16	–	0.49	–	0.35	–	2.81	–
SP6–Cu–A	0.77	–	0.06	–	0.17	–	3.61	–
SP6–Cu–B	0.20	–	0.42	–	0.38	–	2.83	–
SP6–Cu–C	0.08	–	0.33	–	0.59	–	2.49	–

of Mn^{3+} . If the second hypothesis is verified, then the question remains as to which of the two steps is rate limiting, the Mn^{4+} to Mn^{3+} or the Mn^{3+} to Mn^{2+} reduction? To address this question, two biogenic $\delta\text{-MnO}_2$ samples, one produced by an *Acremonium*-like hyphomycete fungus (strain KR21-2) (Miyata et al. 2004) and another by *Leptothrix discophora* (strain SP-6) (Jürgensen et al. 2004), were exposed to the beam, initially at low X-ray fluence to minimize Mn reduction, then for several hours with a full beam to photo-reduce manganese.

The Mn K -edges of the two samples changed shape and the peak maximum shifted to lower energy values as irradiation proceeded (Figs. 6a and 6b). With increasing fluence, the peak position shifted from an Mn^{4+} -like maximum at 6560.7 eV to an Mn^{3+} -like maximum at 6558.2 eV, and its shape became asymmetrical with a shoulder at the Mn^{2+} -like maximum of 6551.8 eV. At moderate reduction, Mn^{3+} increased from 12 to 49% (KR21-Cu-B) and 6 to 42% (SP6-Cu-B), and Mn^{2+} from 11 to 35% (KR21-Cu-B) and 17 to 38% (SP6-Cu-B) (Figs. 6c, 6d, and 7). Further irradiation (sample SP6-Cu-C) continued to increase the amounts of Mn^{2+} , but Mn^{3+} decreased from 42 to 33% at near completion of the Mn^{4+} reduction (8%). The predominance of Mn^{3+} at the beginning of the reaction, followed by the predominance of Mn^{2+} at the end of the reaction, both cations being minor

species in the initial materials, means that only one electron is transferred at a time and the Mn^{3+} to Mn^{2+} step is rate limiting. Structurally, this limiting step likely corresponds to the migration of the reduced Mn^{3+} cations from within the phylломanganate layer to the interlayer region (Silvester et al. 1997).

Application of the Combo method to other materials

The combination fit with a database procedure, or Combo method, presented here may be applied to other Mn materials, with the caveats that non-linearity effects may defeat the interpolation giving unrealistic values or poor data reconstruction. Figure 8 shows with the example of hausmannite (Mn_3O_4) that quite accurate valence fractions still can be obtained empirically if the loadings are constrained to be non-negative, even though the resulting fit is poor: $NSS = 5.2 \cdot 10^{-3}$ compared to $10^{-5} \leq NSS \leq 10^{-4}$ for phylломanganates and tectomanganates (Supplementary Table 2¹). The Combo method yields 67% Mn^{3+} + 28% Mn^{2+} + 5% Mn^{4+} (average 2.76), in fair agreement with the formal valence composition of 2/3 Mn^{3+} and 1/3 Mn^{2+} , and in closer proximity to the actual value of 2.67 than the value of 2.86 derived from a linear fit with only MnO , Mn_2O_3 , and MnO_2 (Fig. 8c). Thus, this method seems to capture some characteristics of the input spectrum that correspond to the valence mixture, which other-

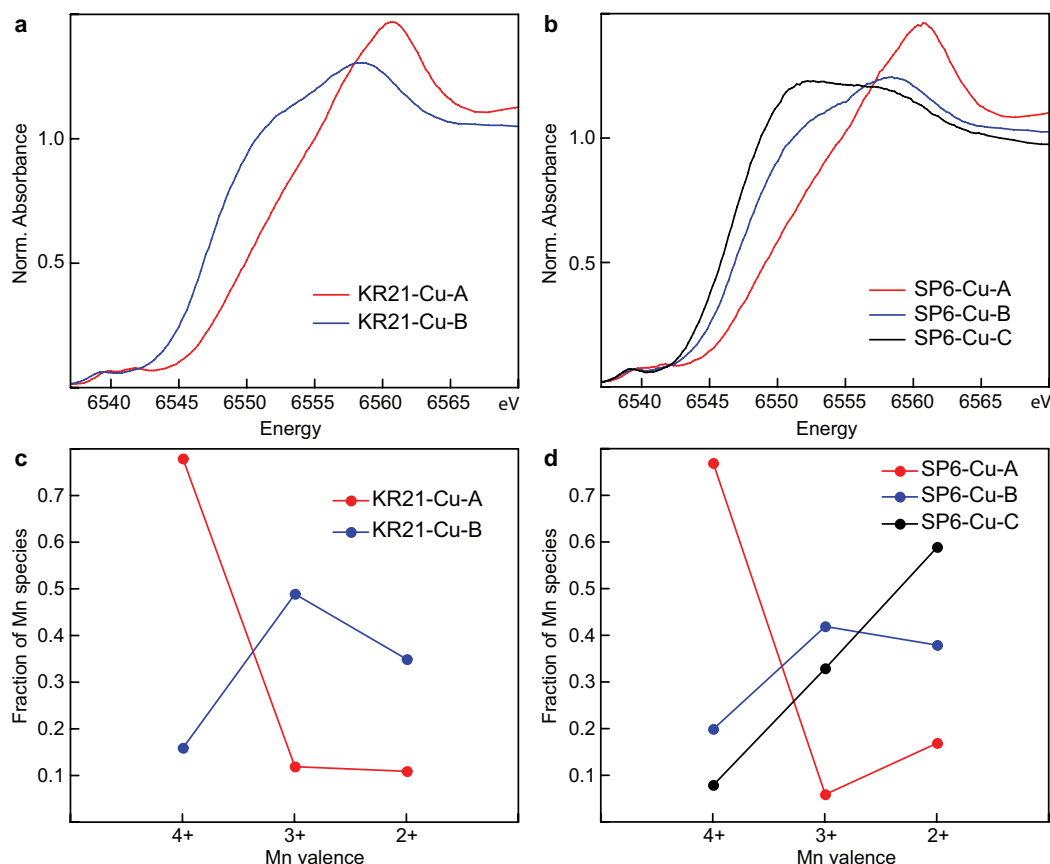


FIGURE 6. (a and b) XANES absorption spectra of two biogenic phylломanganates at low (KR21-Cu-A, SP6-Cu-A), moderate (KR21-Cu-B, SP6-Cu-B), and high (SP6-Cu-C) X-ray fluence. (c and d) Evolution of the fractions of Mn^{4+} , Mn^{3+} , and Mn^{2+} at each accumulated X-ray fluence. The initial fraction of Mn^{2+} not oxidized by the enzymatic oxidation of Mn^{2+} to Mn^{4+} was removed by suspending the undamaged materials in 10 mM CuSO_4 overnight after synthesis, and washing it two times in deionized water (Adams and Ghiorse 1988).

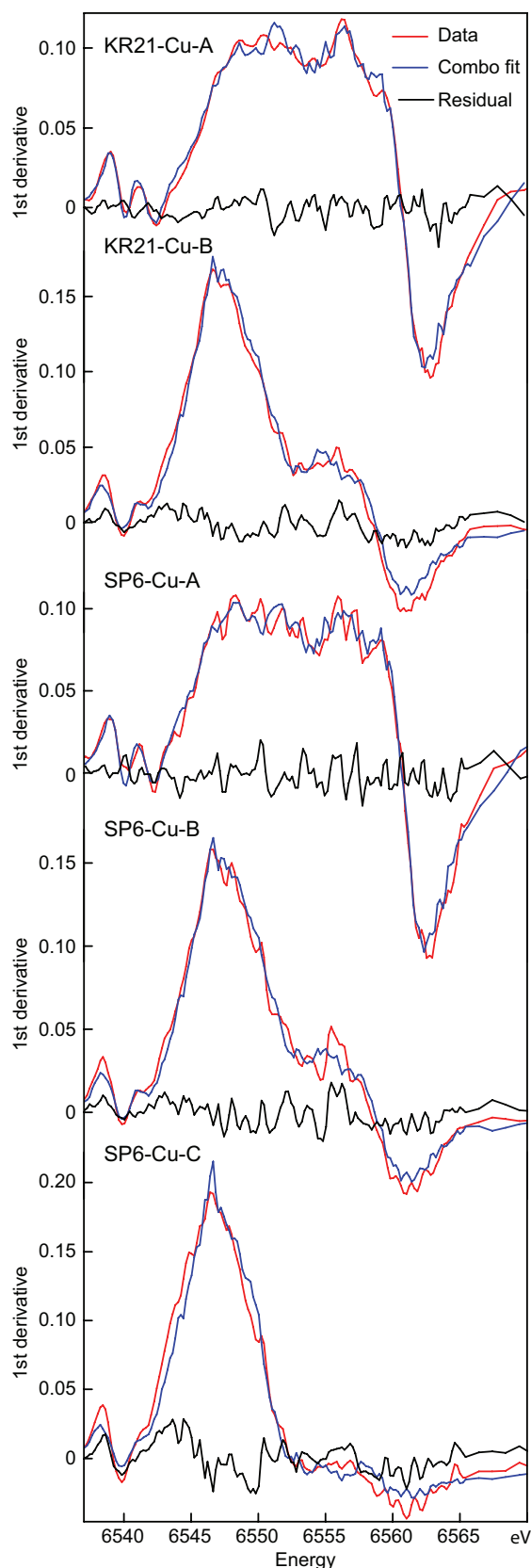


FIGURE 7. Combo fit of the biogenic XANES spectra.

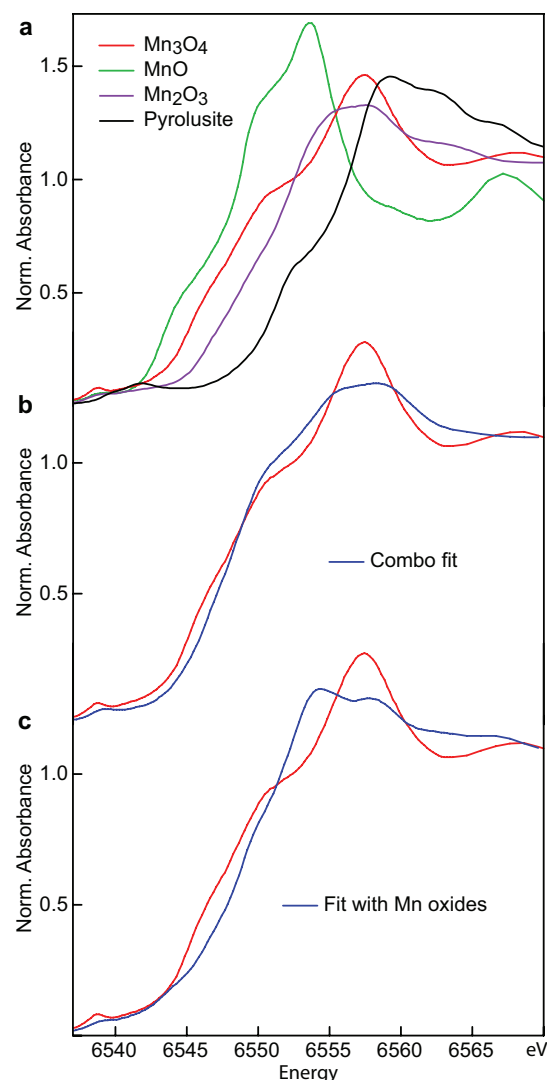


FIGURE 8. (a) XANES absorption spectra of Mn oxides. Best-fit of Mn_3O_4 with the Combo method (b) and with a linear combination of MnO , Mn_2O_3 , and $\beta\text{-MnO}_2$ (pyrolusite) (c). Even when the fit is poor, the actual valence sum (2.67) is better extracted with the Combo method (2.76) than with a linear fit of the best chemically relevant references (2.86).

wise are missed when the regression analysis is conducted with a limited set of model compounds that are chemically close but structurally distinct from the unknown materials.

Comparison with methods based on calibration curves

Continuing with Mn_3O_4 , this mixed-valent oxide can be used to compare the precision of the average valence derived from the proposed method and from the usual calibration method, which correlates the valence to the energy position (or “chemical shift”) of various features in the XANES spectra (Wong et al. 1984; Ressler et al. 1999, 2000; Ramallo-Lopez et al. 2004; Figueroa et al. 2005). An average valence of 2.43 is obtained when the absorption threshold is taken as the energy of the absorbance at $0.4 \leq \Delta\mu \leq 0.8$, and 2.30 from the energy position of the first peak in the derivative curve (Figs. 9a and 9b). These two va-

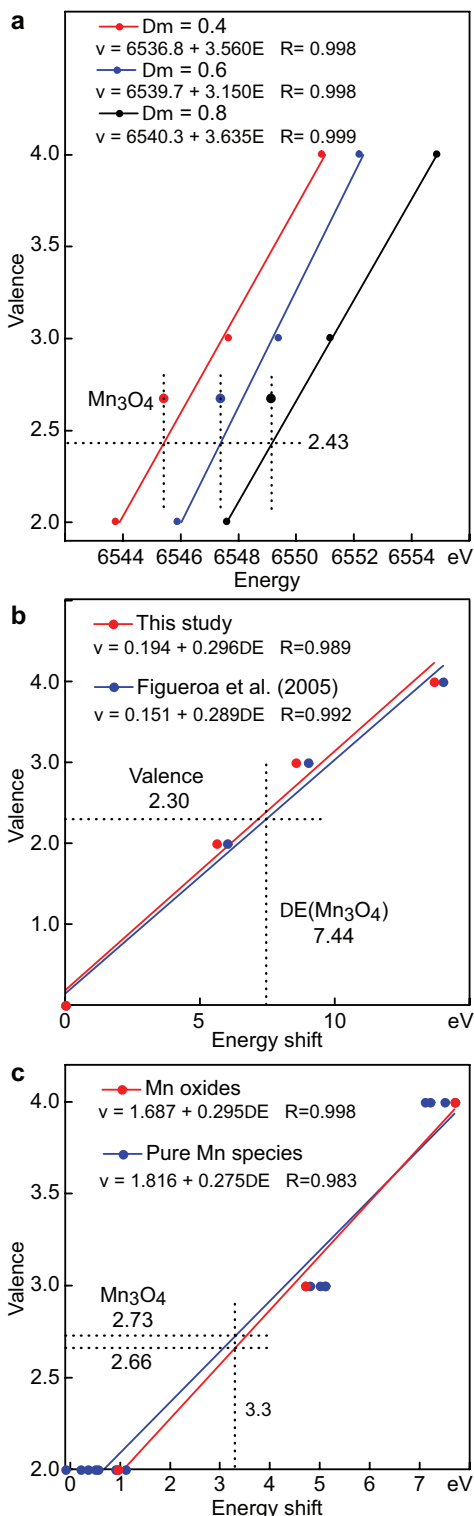


FIGURE 9. Determination of the average Mn valence of hausmannite (Mn₃O₄) using calibration curves calculated with MnO, Mn₂O₃, and MnO₂ (pyrolusite) as calibrants. The curves were calculated from the dependence on valence of the threshold energy at $\Delta\mu = 0.4, 0.6$, and 0.8 (a), the energy of the first peak in the first derivative (b), and the edge shift relative to the Mn foil calculated at 80% of the integrated absorption area [6550.95 eV; method of Capehart et al. (1995)] (c).

lences are further apart from the nominal value of 2.67 than the value of $0.67 \times 3 + 0.28 \times 2 + 0.06 \times 4 = 2.79 \pm 0.02$ derived from the Combo method. Interestingly, the correct value (2.66 ± 0.01) is obtained using the calibration method of Capehart et al. (1995) and MnO, Mn₂O₃, and MnO₂ (pyrolusite) as calibrants (Fig. 9c; Supplementary Table 5¹). When the calibration curve of Capehart is calculated with all the pure-valence references in the database, the average Mn₃O₄ valence is 2.73. Figure 9c shows that the loss in accuracy results from the large variability in the shape of the Mn²⁺ spectra, as seen from the dispersion of the $y = 2$ points on the x (energy) axis. The inclusion in the database of several references with the same oxidation state but a wide range of chemical structures facilitates the determination of the valence fractions by the Combo method, because the irrelevant references give negative loadings. In contrast, in the calibration method the effects of valence, site symmetry, coordination geometry, ligand electronegativity, and bond distances on various absorption features in the XANES spectra all contribute to the slope of the valence = f (energy) straight line. Therefore, the only way to improve tangibly the applicability of the calibration method is to gather independent estimates of the most likely local environments in the unknown material.

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